

FREE-ELECTRON NETWORK MODEL FOR CONJUGATED SYSTEMS. IV[†]

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SUBJECT of this note is (1) to investigate the bond-length against mobile-electron population curve obtained empirically in the second paper of the present series¹ and (2) to make some comments on DE- (delocalization-energy) values. It is possible to derive the empirical equation of the above-mentioned curve by starting with the same considerations which Coulson² used to derive the theoretical form of a similar curve obtained from LCAO MO calculations. Following Coulson, we say the total energy F , which allows for the compression of the σ -bonds, is

$$F = \sum_{\lambda} \frac{1}{2} k_s (x_{\lambda} - s)^2 + \sum_{\lambda} E_{\pi\lambda} ; \quad \partial F / \partial x_{\lambda} \big|_{\text{equil.}} = 0 \text{ for all } x_{\lambda} , \quad (1)$$

where k_s is the single-bond stretching constant, s the ethane carbon-carbon internuclear distance, x_{λ} the length of bond λ , and $E_{\pi\lambda}$ the π -electronic energy of bond λ . To write $E_{\pi\lambda}$ explicitly, we assume (1) that the binding energy of the π -electrons in bond λ is proportional to $b(\lambda)$, the total mobile-electron population in bond λ , and (gratuitously) (2) that the proportionality factor may be taken as the energy that an ethylene bond would have if the ethylene carbon-carbon internuclear distance were equal to x_{λ} . Eq. (1) is based upon the premise that the orbital energies of the occupied levels are negative; of the unoccupied, positive. Hence, the zero reference level of the free-electron orbital energies must be shifted to the level where $\kappa = \frac{1}{2}\pi$.³ We may now rewrite (1) as

[†]This work was assisted in part by the Office of Naval Research under Task Order IX of Contract N6ori-20 with The University of Chicago.

¹C. W. Scherr, J. Chem. Phys. **21**, 000 (1953), hereafter referred to as II. See Fig. 4 and Eq. (7).

²C. A. Coulson, Proc. Roy. Soc. (London) **A169**, 413 (1939).

³This point will be considered in detail by K. Ruedenberg in a forthcoming paper of this series.

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$$\left. \begin{aligned} F &= \sum_{\lambda} \frac{1}{2} k_s (x_{\lambda} - s)^2 + \sum_{\lambda} b(\lambda) E_H (a\pi/x_{\lambda})^2 [(1/9) - (1/4)] , \\ \partial F / \partial x_{\lambda} &= k_s (x_{\lambda} - s) + b(\lambda) E_H (5/18) x_{\lambda}^{-3} a^2 \pi^2 = 0 . \end{aligned} \right\} \quad (2)$$

and
Substituting $E_H = 13.596 \text{ eV}$, ^{4a} $a = 0.529151 \text{ \AA}$, ^{4a} $k_s = 4.50 \times 10^5 \text{ dynes/cm}$, ^{4b} and $s = 1.54 \text{ \AA}$, we obtain for x_{λ} in Angstroms

$$x_{\lambda}^3 (x_{\lambda} - 1.54) + 0.372 b(\lambda) = 0 . \quad (3a)$$

The empirical equation, Eq. (7) of II, may be written as

$$x_{\lambda} = 1.525 - 0.1398 b(\lambda) . \quad (4)$$

Eq. (3a) may be approximately compared with Eq. (4) by setting x_{λ}^3 equal to a mean value, $(1.39)^3$, leading to

$$x_{\lambda} = 1.54 - 0.1385 b(\lambda) , \quad (3b)$$

in a very fine, but perhaps fortuitous, agreement with Eq. (4).

The DE-values for all the molecules treated in II may be computed easily from the tabulated eigenvalues in Table I of that paper. For simplicity one may use the following:

(for condensed hydrocarbons)

$$- \text{DE}(\text{kcal}) = \sum_{i=0}^{\frac{1}{2}n} 90.90 \kappa_i^2 - 49.84n ;$$

(for polyenes)

$$- \text{DE}(\text{kcal}) = \sum_{i=0}^{\frac{1}{2}n} 97.84 \kappa_i^2 - 53.63n ,$$

based on D, the free-electron parameter, equal to 1.39 and 1.34⁰, respectively, and where n is the number of π -electrons. Some of the results are presented in Table I. The results are surprisingly poor, being for small molecules much too large, and occasionally in the wrong order, e. g., styrene and benzene. Non-existent molecules however have satisfactory relatively small DE-values. This failure however is not a

^{4a}J. W. M. DuMond and E. R. Cohen, Amer. Scientist **40**, 447 (1952).

^{4b}G. Herzberg, Infrared and Raman Spectra of Polyatomic Molecules [D. Van Nostrand Co., Inc: New York, 1945], p. 193.

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TABLE I.
CALCULATED DELOCALIZATION-ENERGY VALUES

<u>Molecule</u>	<u>Delocalization Energy</u>		
	Free-electron Model	Eq. 5	Experimental ^a
Butadiene	21.4	-	3.5 ^b
Hexatriene	45.9	-	6.7 ^c
Benzene	99.7	43.2	41
Azulene	103.4	-	46 ^d
Naphthalene	122.0	79.2	77
Anthracene	140.6	115.2	116
Phenanthrene	152.9	115.2	130
Pyrene	146.6	129.6	152
Naphthacene	158.5	144.0	~155 ^e
Triphenylene	189.8	151.2	~158 ^e
Perylene	177.4	172.8	~180 ^f
Styrene	88.2	57.6	51
Diphenyl	158.4	93.8	91
Stilbene	177.9	108.0	101
<u>Non-existent Molecules</u>			
Cyclo-butadiene	-24.9		
Fulvene	36.5		
Pentalene	56.2		
Difulvene	75.8		

^aTaken from reference 5, p. 81, except as noted.

^bHeat of hydrogenation data.

^cHeat of hydrogenation data for cyclo-heptatriene.

^dE. Heilbronner and K. Wieland, Helv. Chim. Acta **30**, 947 (1943).

^{e, f}Estimates made by the present author by a comparison of the heats of combustion reported (e) by A. Magnus and F. Becker, Erdöl u. Kohle **4**, 115-8 (1951) or (f) by J. Syrkin, J. Phys. Chem. USSR **17**, 347 (1943), with reference 5, p. 69.

serious criticism of the theory, since it is well known that there is almost no justification for the "theoretical calculations" of DE-values, other than that they reproduce experiment remarkably well.⁵ In fact the very simple formula

$$DE(\text{kcal}) = 7.2N, \quad (5)$$

⁵See, e. g., G. W. Wheland, The Theory of Resonance [Wiley and Sons: New York, 1944], p. 79.

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where N is the number of bonds in the conjugated system, reproduces the DE-values of the condensed molecules considered in II to within a few kcals (see Table I), so that any theoretical quantity that happens to increase almost linearly with increasing number of bonds would serve to "predict" the DE-values in such cases.
